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Photo-assisted Electrochemical Degradation of Polychlorinated Biphenyls (PCBs) with Boron Doped Diamond Electrodes

The capacity of the photo electro-Fenton (PEF) process to degrade a mixture of seven polychlorinated biphenyl (PCB) congeners (PCB28, PCB52, PCB101, PCB138, PCB153, PCB180 and PCB209), each at an initial concentration of 50 μg L^{-1}, was studied. Boron-doped diamond (BDD) sheets were used as anode and cathode in the experimental electrolytic cell that contained Na_2SO_4 0.05 M at pH 3 as supporting electrolyte for the electro generation of H_2O_2 at the cathode. The effects of UV light intensity (254 and 365 nm), current density (8, 16 and 24 mA cm^{-2}) and the initial concentration of the ferrous ion (0.1, 0.2 and 0.3 mM) on PCB degradation efficiency were evaluated. PCB concentration was monitored with a gas chromatograph coupled to an electron capture detector (GC-ECD). The highest level of degradation of the PCB mixture (97%) was achieved with 16 mA cm^{-2} of current density, 0.1 mM of ferrous ion and UV light at 365 nm as irradiation source after 6 hours of reaction. PCB28, PCB52 and PCB101 were not detected by the chromatographic method after 0.5, 1.5 and 3 h of reaction, respectively. The degradation of PCB138, PCB153, PCB180 and PCB209 was also high (> 95%), reaching a maximum of 97% for PCB 138. The PEF system out performed other advanced oxidation processes, namely electro-Fenton, anodic oxidation, Fenton, photo-Fenton and UV photolysis, in terms of reaction rate and degradation efficiency. These results demonstrate for the first time the degradation of PCB209, the most highly chlorinated PCB congener, by an advanced electrochemical oxidation process.

Keywords: Advanced electrochemical oxidation processes; BDD electrodes; PCB209, Persistent organic pollutants; Photo electro-Fenton system.

1. Introduction

Polychlorinated biphenyls (PCBs) are known for their high toxicity, low biodegradability, for being bioaccumulative and for their potential to be transported over long distances. Due to these characteristics, PCBs have been included in the list of the twelve key persistent organic pollutants by the Stockholm convention.[1] The PCBs family consists of 209 congeners, all of them described by the empirical formula $C_{12}H_{10-n}Cl_n$ (n=1–10) but with different number and position of chlorine atoms in their

molecule. It is estimated that during the time the PCBs were produced, 1.3 to 2 million tons of these compounds were discharged to the atmosphere.[2] By the end of the 1970's, most governments banned the production of PCBs. However, even today widespread environmental contamination persists as a result of accidental spills and leaks that occurred in the past due to improper transportation, storage and disposal of PCBs.[3] The environmental presence of PCBs still represents a serious risk to both the environment and the human health (e.g. it is a risk factor for cancer and genetic mutations).[4] For this reason, a large number of studies aimed at solving this pollution problem has been reported.[1,5-7] The degradation of PCBs has been studied using various chemical and biological processes such as incineration,[8] biodegradation with fungi and bacteria,[9,10] radiolytic degradation using Co^{60} as source of γ rays,[11] as well as some advanced oxidation processes (AOPs).[5,12] However, there are still some limitations in the application of these methods. For example, the incineration of PCBs can produce undesirable products such as dioxins and furanes,[8,13] which are more toxic than the PCBs themselves. Biological processes, despite being widely investigated, have high specificity,[14] and, particularly, treatment times that can be as long as several months.[15] Meanwhile, most of the AOPs that have been studied had been able to degrade only PCBs with a low number of chlorine atoms in their molecule (mono, di-, tri-, tetra-, penta- or hexachlorinated).[1,5,16,17] The AOPs most extensively studied in the degradation of PCBs are the Fenton (F) and the photo-Fenton (PF) systems. With these processes, it has been possible to significantly reduce treatment times from a length of months to days.

In recent years, the traditional set of AOPs has been extended to include novel electrochemical processes such as electro-Fenton (EF), photo electro-Fenton (PEF) and anodic oxidation (AO) systems, among others. The improvements brought about by

these systems are due to the fact that they accomplish a continuous and *in situ* production of the precursor species of the degradation process. This way, the electrochemical advanced oxidation processes (EAOP) can achieve high degradation efficiencies on a broad spectrum of contaminating molecules. For example, these processes have been successfully applied to the degradation of pesticides,[18-20] pigments and dyes,[21,22] and various emerging contaminants such as pharmaceutical[23-25] and personal care products,[26,27] among other molecules. In EAOPs, the electrode material plays an important role in the efficiency of degradation and different alternatives have been used including Pt electrodes, stainless steel, carbonaceous materials, Ag and boron doped diamond (BDD) electrodes. Among the main advantages of BDD are its low capacitance, extreme electrochemical stability and, especially, its wide range of electrochemical potential in non-aqueous and aqueous media [23]. Furthermore, the high potential of such electrodes enables the production of larger amounts of $^{\bullet}OH$ and consequently higher rates and degradation efficiencies. Considering the above, the coupling of the PEF system and BDD electrodes, as both anode and cathode, offers a promising alternative for treating chemically stable molecules such as highly chlorinated PCBs congeners. The objective of this study was to evaluate the degradation of a mixture of seven PCB congeners (PCB28, PCB52, PCB101, PCB138, PCB153, PCB180 and PCB209) using the PEF system with BDD electrodes.

2. Materials and methods

2.1. Reagents

The mixture of standard grade PCBs (PCB28, PCB52, PCB101, PCB138, PCB153, PCB180 and PCB209, $1x10^4$ µg L^{-1} of each one), Na_2SO_4 and H_2SO_4, both analytical

reagent grade, and hexane and methanol, both HPLC grade, were obtained from Sigma-Aldrich. Analytical reagent grade $FeSO_4 \cdot 7H_2O$ and H_2O_2 were supplied by J. T. Baker. Distilled and deionised water was used in the preparation of all aqueous solutions.

2.2. Electrochemical system

The experiments were conducted in an undivided electrolytic cell of 50 mL working volume, filled with Na_2SO_4 0.05 M at pH 3 as supporting electrolyte. This pH value was used since many studies have reported that the optimum pH of the Fenton process is around 3.[28,29] This is because iron species begin to precipitate as ferric hydroxides at higher pH values and form stable complexes with H_2O_2 at lower pH values, leading to deactivation of the catalyst. BDD electrodes (25 x 50 mm bipolar/Si 1 mm; Adamant Technologies, Switzerland), positioned in parallel with 2 cm spacing, were used as anode and cathode. Before starting the oxidation process, the reaction medium was saturated with oxygen by bubbling air at a flow of 300 mL min^{-1} for 45 minutes. Following this, electric current was induced into the system for an hour which enabled the electro production of hydrogen peroxide. Next, the reaction medium was spiked with the mixture of PCBs at a concentration of 50 µg L^{-1} for each of the seven congeners. Soon after, the oxidation process was initiated by adding Fe^{2+} and by irradiating the medium with UV light (λ= 254 and 365 nm). The degradation reaction was carried out for 6 hours, and during this time, the agitation, temperature and air bubbling were maintained at constant values of 850 rpm, 25 ± 2°C and 300 mL min^{-1}, respectively. The degradation of PCBs was monitored by analysing samples of the reaction medium collected every 90 minutes; this analysis was performed by gas chromatography. All glass materials used in the oxidation tests and chromatographic analyses were previously acid washed and heated at 450 °C for 2 h.

2.3. Extraction of PCBs

PCBs were extracted from the aqueous phase using a liquid:liquid extraction method, with a 1:2 sample:solvent (hexane) ratio. This mixture was mixed vigorously for 10 min using a vortex. The recovered organic phase was mixed again with 0.075 g of Na_2SO_4 to remove moisture. Finally, the extract was stored until chromatographic analysis. The recovery percentages obtained with this method are presented in Table 1.

2.4. Chromatographic method

The analysis and quantification of PCB congeners was performed on a Clarus 500 gas chromatograph (Perkin Elmer, Massachusetts, USA) with an electron capture detector (GC-ECD). A MDS-5S glass capillary column (Supelco, Pasadena, USA) of 30 m long, 0.25-mm i.d. and 250-µm film was used. Samples (2 µL) were injected in split less mode. H_2 at 45.0 cm seg^{-1} was used as carrier gas. The temperatures of the injector and detector were set at 280°C and 350°C, respectively. The analysis was conducted using the following oven temperature program: 80°C for 1 minute increased to 200°C with a ramp of 45°C min^{-1}; increased further to 250°C at 3°C min^{-1}, hold for 7 min. The validation of the chromatographic method was performed by determining the accuracy expressed as relative standard deviation (RSD), the linearity between the concentrations of the PCBs and their chromatographic response as denoted by R^2, the limit of quantitation (LOQ) and the limit of detection (LOD). The values obtained for these parameters are shown in Table 1.

[Table 1 near here]

2.5. Analytical methods

The concentration of total iron and ferric ion (Fe^{3+}) was determined using the colorimetric method with phenanthroline, quantifying the complex formed at 510 nm.[30] The concentration of ferrous ion (Fe^{2+}) was calculated from the difference between the concentration of total iron and Fe^{3+}. The residual hydrogen peroxide was also monitored using a colourimetric method with titanium oxysulfate; the coloured complex was quantified at 406 nm. A UV/Vis spectrophotometer SQ-2800 (Cole Palmer) was used for these analyses.

2.6. Statistical analysis

Degradation tests followed a 2x3x3 factorial design, where the UV light intensity (254 and 365 nm) was the first factor, the initial concentration of ferrous ion (0.1, 0.2 and 0.3 mM) was the second factor and the current density (8, 16 and 24 mA cm^{-2}) was the third factor. Statistical analysis of data was performed with Statisitica 7 (StatSoft, Inc.) software with a significance level of 5%.

3. Results and discussion

3.1. Degradation of PCBs by the photo electro-Fenton system

The ANOVA performed on the results of the PCBs degradation tests by the PEF system (Table 2), showed the existence of significant differences among treatments. In this test set, the highest percentage of degradation (97.5±0.2 % of the initial concentration of 350 µg ΣPCBs L^{-1}) was achieved when the system operated with 16 mA cm^{-2} of current density, 0.1 mM Fe^{2+} and UV light of 365 nm (Fig. 1). These results can be explained by the way reactions occur in the PEF system. The PEF process is initiated with the continuous production of H_2O_2 by the reduction of dissolved oxygen via 2 electrons (Eq. 1), which then reacts with the added Fe^{2+} to generate $^{\bullet}OH$ radicals (Eq. 2). Equations 1-2 show that as the current intensity increases, there is a higher generation of

the oxidasing species •OH and, consequently, an increased degradation efficiency due to more •OH being available to react with the saturated and aromatic organic compounds (Eq. 3 and 4, respectively).[31] However, it can also be expected that once certain concentrations of Fe^{2+} and H_2O_2 are reached, the degradation efficiency would start to decline.[31,32] This happens due to the occurrence of collateral reactions that compete for •OH radicals. Reactions shown in Equations 5 and 6 are among the competitive reactions that contribute the most to diminished pollutant degradation efficiency. This system behavior was observed in this study. Degradation efficiency showed a tendency to decrease with increased concentration of Fe^{+2} (Fig 1) which suggests that Fe^{+2} is not only reacting as shown in Eq. 2 but also taking part of the reaction depicted by Eq. 5. It can also be observed from Fig 1 that when current density increased from 8 a 16 mA cm^{-2}, the efficiency of PCB degradation also increased which can be explained by the electro generated H_2O_2 reacting mainly according to Eq. 2. However, when current density increased from 16 to 24 mA cm^{-2}, the degradation efficiency showed a decline probably due to a higher oxidation of H_2O_2 as more •OH radicals become available (Eq. 6).

$$O_2 + 2H + 2e^- \longrightarrow H_2O_2 \quad (1)$$

$$H_2O_2 + Fe^{2+} + H^+ \longrightarrow Fe^{3+} + {}^{\bullet}OH + H_2O \quad (2)$$

$$RH + {}^{\bullet}OH \longrightarrow R^{\bullet} + H_2O \quad (3)$$

$$ArH + {}^{\bullet}OH \longrightarrow ArH({}^{\bullet}OH) \quad (4)$$

$$Fe^{2+} + {}^{\bullet}OH \longrightarrow Fe^{3+} + OH^- \quad (5)$$

$$H_2O_2 + {}^{\bullet}OH \longrightarrow H_2O + HO_2^{\bullet} \quad (6)$$

[Table 2 near here]

[Figure 1 near here]

On the other hand, the rate of degradation of PCBs congeners by the PEF system was inversely proportional to the percentage of chlorination of each molecule (Fig. 2). This behavior has been reported in previous works where other PCB congeners have been degraded with different AOP.[1,5,16,33] The concentration of the PCB28, PCB52 and PCB101 congeners were reduced below the LOD at 30, 180 and 270 min, respectively. Congeners with a higher number of chlorine atoms in their molecules (PCB138, PCB153, PCB180 and PCB209) were still detected in the residue obtained after the degradation process, although their concentrations were below 5% of the initial concentration. At the end of the oxidation process, there was a 96.3% reduction in the initial concentration of PCB209. The observed relationship between the efficiency of degradation and the percentage of chlorination of PCB congeners, is due to the free $^{\bullet}OH$ radicals reacting initially at unchlorinated positions, which decrease when the chlorination percentage increase, while the steric barrier increases.[5,34] This results in a great chemical stability which is characteristic of PCBs molecules. Because of this, previous studies on PCBs degradation using AOPs have focused on the oxidation of congeners with low percentages of chlorination.[1,5] This is the first time to the best of our knowledge that the degradation of the highly chlorinated and stable PCB209 congener by an EAOP is reported.

[Figure 2 near here]

The strength of the PEF system is due to the fact that in this reaction medium various degradation processes such as H_2O_2/UV, H_2O_2/Fe^{2+} and AO, among others, occur simultaneously. In all these, the initial degradation step is the generation of $^{\bullet}OH$ radical, and therefore, all degradation routes are conducted via free radicals. This EF system is enhanced when the reaction medium is irradiated with UV light because it

produces the regeneration of Fe^{2+} from $Fe(OH)^{2+}$ photo reduction (Eq. 7) and from the photolysis of Fe^{3+} complexes with generated carboxylic acids (Eq. 8).[31] This complete system represented by equations 1-8 is known as PEF system.

$$Fe(OH)^{2+} + hv \longrightarrow Fe^{2+} + \cdot OH \quad (7)$$

$$Fe(OOCR)^{2+} + hv \longrightarrow Fe^{2+} + CO_2 + R \quad (8)$$

In the PEF system, H_2O_2 photolysis also occurs (Eq 9). Likewise, water oxidation on BBD electrodes can produce large amounts of $^{\bullet}OH$ radicals (Eq. 10), which remain adsorbed on the anode surface ($^{\bullet}OH_{ads}$). These $^{\bullet}OH$ radicals are capable of reacting with the organic compounds until full mineralisation.[35-37]

$$H_2O_2 + hv \longrightarrow 2^{\bullet}OH \quad (9)$$

$$BDD + H_2O \longrightarrow BDD(^{\bullet}OH) \quad (10)$$

3.2. Concentration profiles during PEF treatment

The concentration profiles of the Fenton reagents and PCBs mixture during PEF treatment are presented in Fig. 3. It can be seen that in the first 30 minutes of reaction, the high rate of consumption of both H_2O_2 and Fe^{2+} corresponds to the highest rate of degradation of the mixture of PCBs. After this initial period, the PCBs degradation rate decreases while the concentration of both H_2O_2 and Fe^{2+} is slightly recovered (see Eqs. 1 and 7-8). This is due to the fact that by lowering the concentration of PCBs (limiting reagent), the probability of collision and reaction of the reactants also decrease. Meanwhile, competing and recombination reactions are favoured, which is manifested in a decreasing rate of degradation of PCBs. On the other hand, the concentration profile of Fe^{3+} has an inverse behavior than that of Fe^{2+}; that is to say, its concentration increases rapidly in the first 30 minutes and then a slight decrease and stabilisation is observed, which is justified by Eqs. 2,7 and 8. The same Figure 3 shows that during the

degradation reaction, pH slightly increased; however, by the end of the reaction period it is still within the range where Fenton type reactions are carried out optimally.[38,39] The monitoring of the potential difference showed that at the end of the reaction a potential of 17.5 V was held, which was 2.4 V below the initial value. This variation can be attributed to the generation of both negative and positive ions during the degradation process, which facilitate the electrical flow between the electrodes. One of these ions can be the Cl^- anion. The release of Cl ions during the photocatalytic treatment of PCB-contaminated soils has indeed been reported.[40] However, Prządo et al [1] found no significant release of chloride ions from the degradation of PCBs by Fenton's reagent. If present in the electrochemical reaction medium, Cl^- anions may favour the formation of oxidising compounds such as HClO, responsible for indirect oxidation reactions.[41]. They may also act as scavengers of hydroxyl radicals.[42] Moreover, the BDD anode can lead to the formation of higher oxidation states of chlorine, i.e., chlorite, chlorate and perchlorate.[41]

[Figure 3 near here]

3.3. UV light effect

The concentration profiles of H_2O_2, Fe^{2+} and Fe^{3+} in the reaction medium, both in the EF and the PEF system, are presented in Figure 4. In both cases, the electro production of H_2O_2 was carried out under similar conditions (16 mA cm^{-2}, 300 mL air min^{-1}), thus the initial concentrations were approximately the same in both systems. However, it can be seen from Figure 4 that during the reaction period, H_2O_2 concentration was lower in the PEF than in the EF system. This could be the result of the photolysis of the H_2O_2 in the former system, as represented by Eq. 9, which do not occur when the system is not photo-assisted. Therefore, the continuous generation (Eqs. 7,8) and reaction (Eq. 2) of

Fe^{2+} ion with H_2O_2 in the Fenton system, on one side, and the photolysis of H_2O_2 (Eq. 9), on the other, can explain the higher consumption of H_2O_2 in the PEF system. Furthermore, these same reactions (Eq. 7 and 9) explain an additional route generating $^{\bullet}OH$, which could increase the rate of degradation of PCBs in the photo-assisted system.

The behaviour of the Fe^{2+} ion is also observed in Figure 4. In the EF system, Fe^{2+} concentration decreases during the reaction time, while in the PEF system a slight increase in its concentration is observed after the first 30 minutes of the reaction, which can be explained according to Eqs. 7-8.

[Figure 4 near here]

3.4. Degradation process kinetics

The degradation of the PCBs mixture in the PEF system followed pseudo first order kinetics (Table 3), which has also been observed when AOPs have been applied to the degradation of other molecules.[18,43] The regression coefficients (R^2) presented in Table 3 confirm that the experimental data is well described by this type of reaction kinetics. As noted before, it has been reported on numerous occasions [1,5] the existence of an inverse relationship between the degree of chlorination and the degradability of the PCBs. The decrease in the values of the pseudo first order kinetic coefficients (K) as the level of chlorination increase (Table 3) show that the degradation of the PCB mixture generally fits the reported trend. However, there are two apparent exceptions. It can be seen that PCB101, with five chlorine atoms in its atomic structure, apparently degrades slower than PCB138, with six chlorine atoms. This can be the result of PCB101 being removed during the treatment process but also simultaneously produced, as an intermediary product, from the dechlorination of PCB congeners with six or more chlorine atoms in their structure such as PCB153, PCB180 and PCB209.

This would explain why after 30 min of reaction, the concentration of PCB101 is higher than that of PCB138 (Fig. 2). A similar case happens with PCB153 and PCB180, although the concentration difference observed is much lower than in the case described above. This behavior is consistent with previous reports.[44]

[Table 3 near here]

3.5. Comparison of the PEF system with other AOPs

In order to compare the efficiency of the PEF system in degrading the PCBs mixture, additional tests were performed with other AOPs. The processes evaluated were F, EF, PF, AO, H_2O_2/UV and direct photolysis (DP) of PCBs. In the Fenton reaction, the initial concentration of H_2O_2 was 12.5 mg L^{-1} and 0.1 mM of Fe^{2+} ion. In AO a current density of 16 mA cm^{-2} was applied, and in the case of photo-assisted systems UV light at 365 nm was used. These conditions were similar to those that allowed the highest PCBs removal in the PEF system. The degradation profile for each of the evaluated processes is presented in Figure 5. With the exception of DP, the degradation profile of the evaluated processes was adjusted to a pseudo first order kinetic. The kinetics coefficient values obtained in each process (Table 4) demonstrate that the PEF system presented the highest degradation rate (k = 0.0191 L μg^{-1} h^{-1}).

[Figure 5 near here]

[Table 4 near here]

Among the evaluated processes, the DP presented the lowest degradation percentage (2.5 %). With this system, only the PCBs congeners with a low chlorination percentage were degraded.[9] This is because degradation is only promoted by the energy input from the UV light during the reaction. In the H_2O_2/UV system, the

photolysis of both the PCBs mixture and H_2O_2 occurs (Eq. 5). The latter results in a second degradation route via free radicals. For this reason, the H_2O_2/UV system achieved a higher degradation percentage (21.5 %) compared to DP. In the AO system, BDD sheets were used as electrodes since BDD is considered as the best material for a non-active anode, due to its weak interaction with the $^{\bullet}OH$ generated according to Eq. 10.[23] With this system, a degradation percentage of 40.2% was achieved. The low degradation percentage is due to the fact that degradation in this process mainly depends on the probability of collision between a mobile species (i.e. PCB congeners) and the anode surface. This probability decreases as the concentration of mobile species is reduced.

The Fenton systems presented the highest removal percentages. The achieved degradation percentage was 45% with the F system, 49.6% with the PF system and 74.1% for the EF system. This is because in these systems, $^{\bullet}OH$ radicals are dispersed in the reaction medium, which increases the probability of collision and reaction between them and the PCBs, consequently, the removal efficiency increases. The kinetic coefficients analysis (Table 4) shows that PEF, besides reaching the highest degradation percentage, also presented the highest degradation rate. The limiting factor in both F and PF systems is the availability of Fenton reagents which are depleted as reaction progress and hence the generation of $^{\bullet}OH$ radicals also decreases. This limitation is not present in the PEF system where a continuous generation of H_2O_2 occurs, as in the EF. The advantage of the PEF system is that the UV light energy supplied to the system results in an additional degradation pathway,[45] and also causes the reduction of Fe^{3+} to Fe^{2+} which maintains high concentrations of the Fenton reagents. This explains why, compared to other AOPs, the PEF system achieved the highest percentage and rate of PCBs degradation.

The energy consumption (EC) for each process was calculated according to Eq. 11 [18].

$$EC = \frac{VIt}{m_i - m_f} \quad (11)$$

Where,

EC: energy consumption per unit mass of PCB removed, Kwh μg^{-1}

V: potential difference between electrode, V

I: applied current, Amper

t: electrolysis time, hour

m_i: mass of initial PCBs, µg

mf: mass of final PCBs, µg

The energy consumption for 300 minutes of electrolysis is shown in Table 5. In line with their higher efficiency in the removal of PCBs, the Fenton processes showed a lower energy consumption when comparted to the anodic oxidation or the H_2O_2/UV systems. Among the Fenton processes, electro Fenton was the most energy efficient in removing PCBs. The photo-assisted Fenton processes where less energy efficient which shows that the improvement in PCB degradation brought about by UV light irradiation comes at a high energy expense. Overall, the EC of the evaluated systems was much higher than those reported for the five-minutes degradation of a pesticide (6.71×10^{-9} – 54.17×10^{-9} kWh µg pesticide).[18] This difference can be explained by the lower initial concentrations of the PCBs and their higher recalcitrance which required a much longer treatment time.

[Table 4 near here]

4. Conclusions

The PEF system, operated with a current density of 16 mA cm^{-2}, 0.1 mM Fe^{2+} and UV light at 365 nm, efficiently degraded seven PCBs congeners with an initial total concentration of 350 µg L^{-1}. With this system, it was possible to reduce the treatment time reported in previous studies from days to hours. It was also possible to degrade the most highly chlorinated congener (i.e. PCB209). This is the first report of PCB209 degradation by an electrochemical advanced oxidation process. This system proved to be the most efficient for PCBs degradation compared to the anodic oxidation and other types of Fenton systems evaluated.

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Table 1. Analytical method validation parameters. RSD: Relative standard deviation, LOD: Limit of detection, LOQ: Limit of quantitation.

Congener	R^2	% Recovery	RSD	LOD (µg L^{-1})	LOQ (µg L^{-1})
28	0.9512	97	2.54	0.1227	0.2971
52	0.9877	96	5.73	0.1060	0.2568
101	0.909	96	5.53	0.0493	0.1194
138	0.9787	98	1.75	0.0271	0.0657
153	0.9842	99	3.31	0.0252	0.0611
180	0.9787	98	1.6	0.0159	0.0386
209	0.9835	98	2.28	0.0248	0.0602

Table 2. ANOVA of oxidation tests results with PEF system. SS: Sum of Squares, DF: Degrees of Freedom, MS: Mean Square, F: F distribution, p: Probability.

Variation source	SS	DF	MS	F	p
Current Density	128.544	2	64.27	5.74	0.007
UV light intensity (Wavelength)	3.479	1	3.48	0.31	0.581
Fe^{2+} concentration	734.943	2	367.47	32.81	<0.001
Current Density*Wavelength	137.705	2	68.85	6.15	0.005
Current Density*Fe^{2+} Conc.	119.732	4	29.93	2.67	0.047
Wavelength*Fe^{2+} Conc.	150.992	2	75.50	6.74	0.003
Curr. Density*Wavelength*Fe^{2+} Conc.	214.100	4	53.53	4.78	0.003
Residual	403.165	36	11.20		
Total	1893.661	53	35.71		

Table 3. Apparent kinetic coefficients of the PEF system, using a current density of 16 mA cm^{-2}, 0.1 mM of Fe^{2+} and UV light of 365 nm.

	1st Order		Pseudo 1st Order	
Congener	K (h^{-1})	R^2	K (L μg^{-1} h^{-1})	R^2
PCB28	-	-	-	-
PCB52	5.13	0.9673	0.2259	0.9022
PCB101	1.77	0.8807	0.0721	0.9992
PCB138	1.68	0.6737	0.1008	0.8384
PCB153	1.0695	0.7986	0.0305	0.9326
PCB180	1.1502	0.8385	0.0354	0.9692
PCB209	0.9958	0.7962	0.0262	0.9229
Mixture	1.137	0.7922	0.0191	0.9024

Table 4. Kinetic coefficients (k) of pseudo first order of each of the evaluated systems.

	System					
	PEF	EF	PF	F	AO	H_2O_2/UV
K ($L\ \mu g^{-1}\ h^{-1}$)	0.0191	0.0097	0.0037	0.0024	0.0013	0.0008

PEF: photo electro-Fenton, EF: electro-Fenton, PF: photo Fenton, AO: anodic oxidation

Table 5. Energy consumption (EC) of each of the evaluated systems.

	System				
	PEF	EF	PF	AO	H_2O_2/UV
EC (kWh μg^{-1} PCBs)	14.6×10^{-5}	9.7×10^{-5}	13.8×10^{-5}	17.9×10^{-5}	32.0×10^{-5}

PEF: photo electro-Fenton, EF: electro-Fenton, PF: photo Fenton, AO: anodic oxidation

Figure 1. PCBs degradation efficiency (%) by the photoelectron-Fenton system (C_0=350 µg PCBs mixture L^{-1}).

Figure 2. PCBs mixture degradation profile with the PEF system. The system was operated with current density of 16 mA cm^{-2}, UV light of 365 nm and 0.1 mM of Fe^{2+}. The initial concentration of each congener was adjusted to 50 µg L^{-1}.

Figure 3. PEF system conditions along the degradation reactions. Initial concentration of the PCBs mixture was 350 µg L^{-1}. The system was operated with 16 mA cm^{-2}, 0.1 mM of Fe^{2+} and UV light of 365 nm. (□) pH, (△) Potential difference, (▽) Fe^{3+}, (○) Fe^{2+}, (▲) H_2O_2, (◊) PCBs residual.

Figure 4. Concentration profiles of hydrogen peroxide and iron. (a) EF system: (■) H_2O_2, (●) Fe^{2+}, (▲) Fe^{3+}. (b) PEF system: (□) H_2O_2, (○) Fe^{2+}, (△) Fe^{3+}.

Figure 5. PCBs degradation profile with AOP, (●) PEF system, (○) EF system, (▼) PF system, (△) F system, (■) AO, (□) H_2O_2/UV, (◆) DP. The initial concentration of the mixture was adjusted to 350 µg L^{-1}.

Figure 1

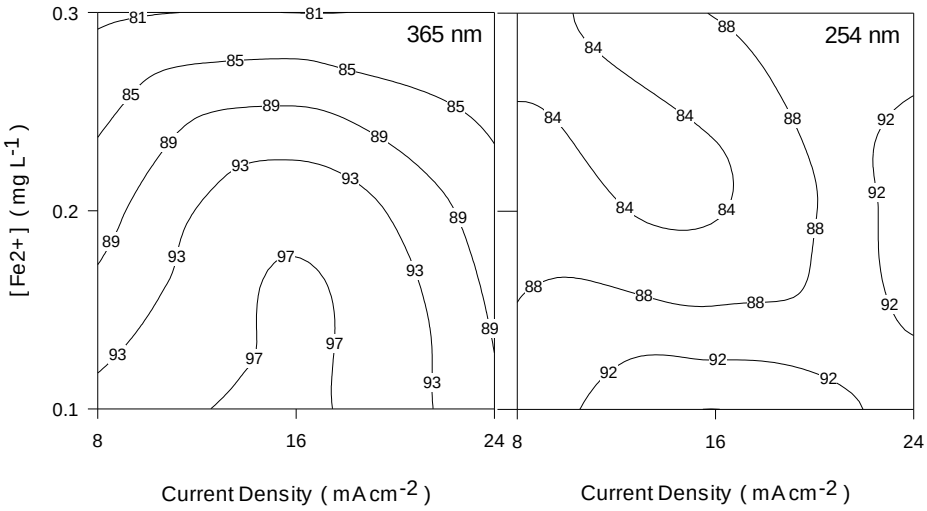

Figure 2

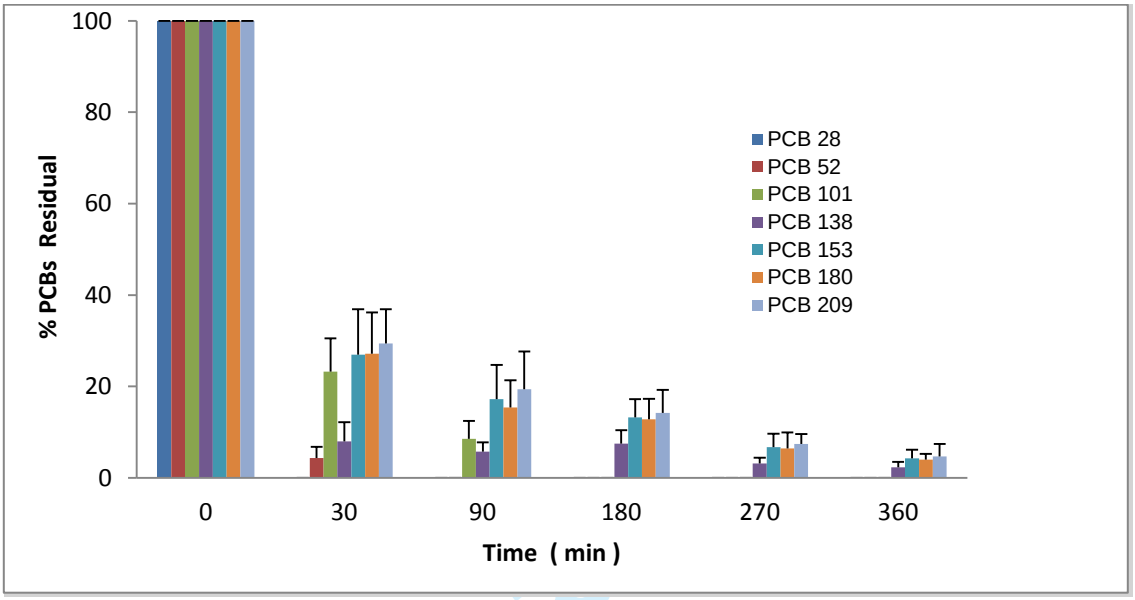

Figure 3

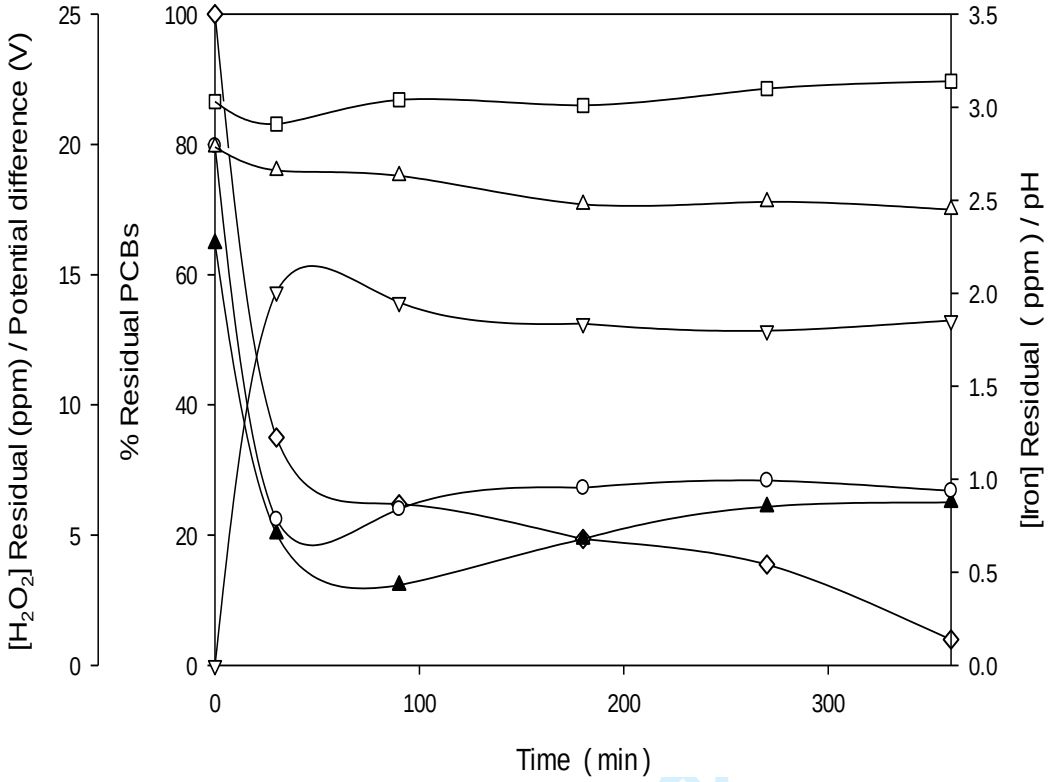

Figure 4

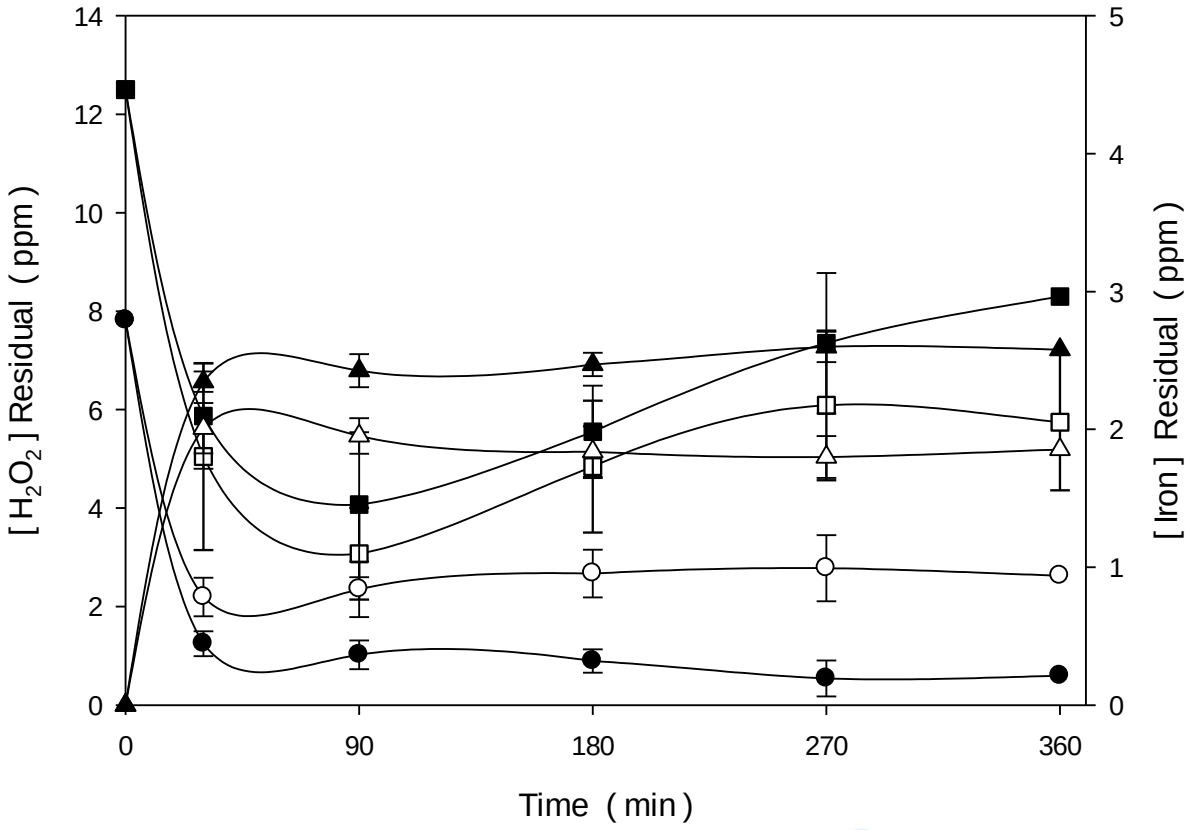

Figure 5